

Two New Silver Coordination Polymers Constructed from 3,3-Azodibenzoic Acid and Different Pyridine Derivatives: Syntheses, Structures and Fluorescent Properties

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ABSTRACT Two coordination polymers (CPs), $\{[\text{Ag}(\text{ADA})_{0.5}(\text{DPE})]\text{H}_2\text{O}\}_n$ (**1**) and $\{[\text{Ag}(\text{ADA})_{0.5}(\text{Bipy})_{0.5}]\text{H}_2\text{O}\}_n$ (**2**), (H_2ADA = 3,3-azodibenzoic acid, DPE = 1,2-di(4-pyridyl)-ethylene, Bipy = 4,4'-bipyridine), have been synthesized via solvothermal reactions of Ag^+ with ADA^{2-} and/or DPE , Bipy . CPs **1** and **2** were characterized by elemental analyses, IR spectra, thermal behaviors, and X-ray single-crystal diffraction. CPs **1** and **2** feature “ $\text{Ag}\cdots\text{Ag}$ ” subunits. CP **1** shows a 3D construction, in which the “ $\text{Ag}\cdots\text{Ag}$ ” subunits extend through ADA^{2-} and DPE ligands using $\mu_6\text{-kO;O;kO;kO;O;kO;kO}$ and $\mu_2\text{-kO;kO}$ coordination modes, respectively. It crystallizes in triclinic system, space group $P\bar{1}$, with $a = 0.3808(18)$, $b = 1.2476(6)$, $c = 1.309(6)$ nm, $\alpha = 76.757(5)^\circ$, $\beta = 84.649(5)^\circ$, $\gamma = 86.809(5)^\circ$; $V = 0.6024(5)$ nm³, $Z = 2$, $M_r = 351.11$, $\text{C}_{13}\text{H}_{11}\text{AgN}_2\text{O}_3$, $D_c = 1.936$ g/cm³, $F(000) = 348$, $S = 1.064$, $R = 0.0323$ and $wR = 0.0689$. CP **2** exhibits a 3D supramolecular structure, in which the “ $\text{Ag}\cdots\text{Ag}$ ” subunits are connected by ADA^{2-} and DPE ligands with $\mu_6\text{-kO;kO;kO;O;kO;kO}$ and $\mu_2\text{-kO;kO}$ coordination modes, respectively. Ultimately, through hydrogen bond and $\pi\cdots\pi$ interaction, the “ $\text{Ag}\cdots\text{Ag}$ ” subunits stabilize the 3D supramolecular structure of **2**. It crystallizes in monoclinic, space group $C2/c$, with $a = 25.301(15)$, $b = 13.197(8)$, $c = 6.970(4)$ nm, $\beta = 102.597(7)^\circ$; $V = 2.271(2)$ nm³, $Z = 8$, $\text{C}_{12}\text{H}_{10}\text{AgN}_2\text{O}_{2.50}$, $M_r = 330.09$, $D_c = 1.931$ g/cm³, $F(000) = 1304$, $S = 1.082$, $R = 0.1107$ and $wR = 0.2984$. The fluorescence properties of CPs **1** and **2** have been also investigated.

Keywords: silver; CPs; synthesis; structure; fluorescence properties;

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1 INTRODUCTION

In recent years, the construction of CPs mainly depends on balance on metal ions and

multidentate ligands under suitable reaction conditions, including reaction temperature, pressure, solvent, *etc*^[1-3]. However, the structures of CPs based on flexible ligands are difficult to predict because of the conformational diversity of different reaction conditions, and the ligands influence the architectures which are largely considered to be serendipitous^[4, 5]. In fact, it is important that the architectures of CPs are achieved via the ligands with some flexible structure units, such as “-X-X-” (X = C, N, O or *etc*). So far, many kinds of flexible ligands with “-X-X-” type unit with metal ions have been reported. There are CPs of ligands with flexible “-C-C-” types documented^[6]. A series of CPs have been synthesized via 3,3'- and 4,4'-dithiobisbenzoic acid ligands with “-S-S-” type unit^[7], as the biphenylethene-4,4'- dicarboxylate ligands containing “-C=C-” type unit bridge the Zn²⁺ or Cd²⁺ centers to produce CPs in the previous researches^[8]. A sequence of compounds with flexible ligands containing “-N=N-” type unit has been reported recently^[9]. Especially, the imidazole and pyridine flexible ligands containing “-X-X-” or “-X-X-X-” units bridging the metal ion centers in the synthesis of complexes have been reported^[10-15]. The ligand with flexible unit can give rise to the construction of frameworks with different structures.

Metallic silver and its complexes as new functional materials have potential applications, such as medical, fluorescence, ion exchange, catalysis, gas adsorption and separation, and so on^[16-19]. Recently, the study of fluorescent properties about silver complexes has relatively extensive research. To achieve useful luminescent Ag-CPs, an effective method is to use the ligand-based strategy, arising from π -conjugated rigid organic ligands. To date, a variety of luminescent Ag-CPs have been reported on organic molecules, however, most of them were focused on the rigid ligands. Only several Ag-CPs have been investigated based on the ligands containing flexible “-X-X-” structure unit.

Bearing the aforementioned ideas and taking advantages of the structures and properties of Ag-CPs, the ligand of 3,3-azodibenzoic acid, and/or 1,2-di(4-pyridyl)ethylene, 4,4'-bipyridine was selected in this work. Fortunately, solvothermal reactions to the mixed ligand with AgNO₃ in different mixed solvent system, pressure and temperature produced two new CPs {[Ag(ADA)_{0.5}(DPE)] H₂O}_n (**1**) and {[Ag(ADA)_{0.5}(Bipy)_{0.5}] H₂O}_n (**2**), which were characterized by elemental analyses, single-crystal diffraction analysis, IR spectroscopy, and thermogravimetric analyses. In addition, the fluorescence properties of **1** and **2** under solid powder state have been investigated at room temperature.

2 EXPERIMENTAL

2.1 Materials and methods

All available solvents and starting materials of analytical grade in the experiments were purchased and used without further purification. Elemental analysis (C, H, N) was determined on a Perkin-Elmer 2400 type elemental analyzer. The infrared spectra were measured between 4000~400 cm^{-1} on a Bruker EQUINOX-55 spectrophotometer using KBr pellets. Thermal decomposition behaviors were performed under nitrogen at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ using a NETZSCH STA 449C thermogravimetric analyzer. The photoluminescence of the solid samples was performed on an Edinburgh Instrument FLS920 fluorescence spectrometer at ambient temperature.

2.2 Syntheses of {[Ag(ADA)_{0.5}(DPE)] H₂O}_n (1) and {[Ag(ADA)_{0.5}(Bipy)_{0.5}] H₂O}_n (2)

{[Ag(ADA)_{0.5}(DPE)] H₂O}_n (**1**) H₂ADA (0.1 mmol), DPE (0.13 mmol), AgNO₃ (0.2 mmol), and 15 mL deionized water were sealed in a 25 mL Teflon-lined stainless-steel autoclave reactor. After stirring for 30 min at room temperature and heated at 160 $^{\circ}\text{C}$ for 96 hours under autogenous pressure, the reaction system was cooled to room temperature at a cooling rate 2 $^{\circ}\text{C h}^{-1}$. The colorless bulk crystals were collected in 43% yield (based on Ag). H, C and N elemental analyses Calcd. (%) for C₁₃H₁₁AgN₂O₃ (**1**): H, 3.16; C, 44.47; N, 7.98. Found (%): H, 3.12; C, 44.52; N, 7.87.

{[Ag(ADA)_{0.5}(Bipy)_{0.5}] H₂O}_n (**2**) A mixture of H₂ADA (0.1 mmol), Bipy (0.13 mmol), AgNO₃ (0.2 mmol), and H₂O (15 mL) was sealed in a Teflon-lined stainless-steel vessel (25 mL) and heated to 170 $^{\circ}\text{C}$ for 3 days under autogenous pressure and cooled to room temperature at a rate of 5 $^{\circ}\text{C h}^{-1}$. Colorless bulk crystals of **2** were obtained in the yield of 30% based on Ag. Elemental analysis calcd. (%) for C₁₂H₁₀AgN₂O_{2.5}: C, 43.66; H, 3.05; N, 8.49. Found (%): C, 43.70; H, 3.10; N, 8.43.

2.3 X-ray crystal structure determination

Crystallographic data for CPs **1** and **2** were collected on a Bruker Smart CCD X-ray diffractometer equipped with graphite-monochromatized MoK α radiation with an ω -scan mode. A semi-empirical absorption correction was applied using the SADABS program^[20]. The structures

were solved by direct methods and refined on F^2 by full-matrix least-squares using SHELX-97^[21, 22]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of coordinated and uncoordinated water molecules were located in a difference Fourier map, while other hydrogen atoms were included in the calculated positions and refined with isotropic thermal parameters riding on the parent atoms. Selected bond lengths and bond angles for CPs **1** and **2** are listed in Table 1.

3 RESULTS AND DISCUSSION

3.1 Crystal structure of CP $\{[\text{Ag}(\text{ADA})_{0.5}(\text{DPE})] \cdot \text{H}_2\text{O}\}_n$ (**1**)

CP **1** crystallizes in the triclinic space group $P\bar{1}$. As depicted in Fig. 1a, the asymmetric unit of CP **1** contains one Ag^+ , one half ADA^{2-} anionic ligand, one DPE ligand, and one coordinated water molecule. Each Ag^+ ion is five-coordinated in distorted tetragonal pyramidal geometry by four oxygen atoms (O(1), O(1)#1, O(1)#2, O(2)) from three ADA^{2-} anionic ligands and one nitrogen atom (N(2)) from one DPE ligand. One oxygen atom (O(1)#1) is at the vertex position of the tetragonal pyramid geometry. The Ag–O/N bond lengths are 2.420(3), 2.375(3), 2.600(3), 2.738(3) and 2.243(3), respectively, which are all in conformity with those in the reported CPs^[23]. It is noted that each Ag^+ ion is connected by three oxygen atoms (O(1), O(1)#1, O(1)#2) to form a 1D ladder chain with the Ag \cdots Ag separations of 3.1365(10) and 3.7484(11) Å. Obviously, there has weak Ag \cdots Ag interaction in the 1D chain^[23]. On the other hand, each ADA^{2-} anionic ligand adopts a $\mu_6\text{-kO,O:kO:kO:kO,O:kO:kO}$ coordination mode, linking adjacent 1D chains via Ag^+ centers to generate a 2D structure in the *ac*-plane (Fig. 1b). The DPE ligands adopt a $\mu_2\text{-kO:kO}$ coordination mode to link the adjacent 2D structures. Thus, the Ag^+ centers, 6-connected ADA^{2-} , and 2-connected DPE ligands link each other to form a 3D framework of CP **1** (Fig. 1c).

3.2 Crystal structure of $\{[\text{Ag}(\text{ADA})_{0.5}(\text{Bipy})_{0.5}] \cdot \text{H}_2\text{O}\}_n$ (**2**)

X-ray single-crystal diffraction analysis shows that CP **2** is a 2D structure, and it extends into a 3D supramolecular compound via hydrogen bonding and $\pi\cdots\pi$ interaction. CP **2** crystallizes in the monoclinic crystal, space group $C2/c$. The asymmetric unit of CP **2** consists of one Ag^+ , one half ADA^{2-} , one Bipy ligand, and one uncoordinated water molecule (Fig. 2a). Each Ag^+ ion is five-coordinated by one N(2) atom from one Bipy ligand, three carboxylate oxygen atoms (O(1),

O(1)#2, O(2)#1) from three ADA²⁻, and one Ag(1)#1 ion. The coordination geometry of each Ag⁺ ion can be described as a slightly distorted tetragonal pyramid, and four atoms (O(1)#1, O(2)#1, Ag(1)#1, N(2)) locate at the plane positions. The Ag–O/N bond lengths vary from 2.234(8) to 2.913(2) Å, and the Ag–Ag bond length is 2.892(2) Å, which are all in agreement with the corresponding values of reported CPs^[23]. As shown in Fig. 2b, the Ag–Ag units are bridged by carboxyl oxygen atoms (O(1)–C(1)–O(2)) of ADA²⁻ ligands to form 1D chains with the 8-membered rings in the *c*-axis direction, and the shortest distance for the 8-membered rings is 14.6184(61) Å on the same plane. Adjacent 1D chains of **1** are linked by the ADA²⁻ and Bipy ligand using μ_6 -kO,O:kO:kO:kO,O:kO:kO and μ_2 -kO:kO coordination modes to generate a 2D structure (Fig. 2c). The hydrogen bonding and $\pi \cdots \pi$ stacking exist in the neighboring 2D structure of CP **2**, which play a critical role in the formation and stabilization of the 3D supramolecular structure (Fig. 2d). The geometrical parameters of all hydrogen bond and $\pi \cdots \pi$ stacking are listed in Table 2.

3.3 IR spectra

The IR spectra display characteristic absorption bands for water molecules, carboxylate, and phenyl units. As shown in Fig. 3, CPs **1** and **2** show broad absorption bands at 3405 and 3472 cm⁻¹, respectively, indicating the presence of ν_{O-H} stretching frequencies of coordinated water molecules. The strong bands at 1690 and 1677 cm⁻¹ are the characteristic stretching vibration of COO⁻ of CPs **1** and **2**. The characteristic IR bands of the phenyl ring bands at 813 and 826 cm⁻¹ are due to the δ_{C-H} vibrations for **1** and **2**, respectively.

3.4 Thermogravimetric analyses

The thermal analysis curves of **1** and **2** were investigated. The first weight loss of 5.20% observed from 70 to 240 °C for **1** corresponds to the release of water molecule (calculated 5.13%). It keeps losing weight from 260 to 410 °C due to the departure of ADA²⁻ and DPE ligands. The final residue of 33.71% is close to the calculated value of 33.00% based on Ag₂O. The first weight loss of 5.53% below 220 °C of **2** results from the loss of water molecules (calculated 5.45%). Above 470 °C, a plateau region is observed, implying that the ADA²⁻ and Bipy ligands are decomposed, with the final residue to be Ag₂O (found 35.19%, calcd. 35.10%).

3.4 Photoluminescence properties

The fluorescence properties of CPs **1** and **2** were examined at room temperature in the solid

state. As shown in Fig. 4, an intense emission of the H₂ADA ligand occurs at 415 nm with an excitation wavelength of 360 nm, which can be attributed to $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transitions. CPs **1** and **2** exhibit the maximum emission peaks at 421 and 419 nm in broad bands when excited at 376 and 359 nm, and which are red-shifted by 6 and 4 nm for the H₂ADA ligand, respectively. However, the emissions of CPs **1** and **2** can be attributed to neither metal-to-ligand nor ligand-to-metal charge transfer because the Ag⁺ ion is in d^{10} configuration and difficult to oxidize or reduce^[24]. Therefore, this may be assigned to intraligand $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transitions.

4 CONCLUSION

Two new CPs, {[Ag(ADA)_{0.5}(DPE)] H₂O}_n (**1**) and {[Ag(ADA)_{0.5}(Bipy)_{0.5}]H₂O}_n (**2**), have been synthesized by hydrothermal method, and their structures were determined and characterized by single-crystal X-ray diffraction analysis, elemental analysis, IR spectroscopy, and thermal behaviors. The crystal structure of CP **1** is a 3D framework consisting of Ag⁺ centers, 6-connected ADA²⁻ anionic ligand (μ_6 -kO,O:kO:kO:kO,O:kO:kO) and 2-connected DPE ligands (μ_2 -kO:kO). CP **2** is a 3D supramolecular structure. The Ag-Ag subunits are bridged to form 1D chains, and adjacent 1D chains are linked by the ADA²⁻ (μ_6 -kO,O:kO:kO:kO,O:kO:kO) and Bipy (μ_2 -kO:kO) ligand to generate 2D structures. The hydrogen bonding and $\pi \cdots \pi$ stacking interactions existing in the neighboring 2D structures play a critical role in forming and stabilizing the 3D supramolecular structure (Fig. 2d). Furthermore, solid-state photoluminescence measurements show that CPs **1** and **2** produce strong emissions at room temperature.

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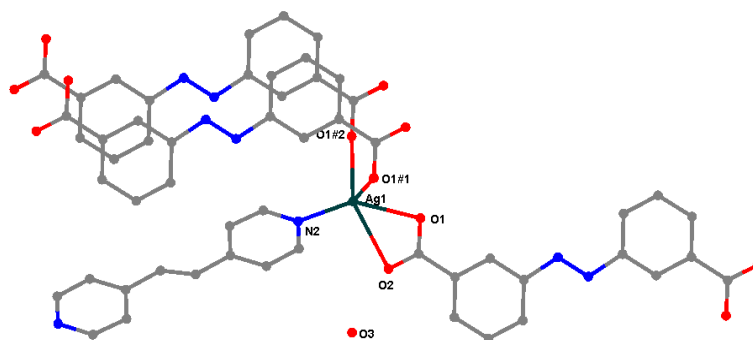


Fig. 1a. Asymmetric unit of complex 1. Symmetry codes: #1: $-x, 2-y, 1-z$; #2: $1-x, 2-y, 1-z$

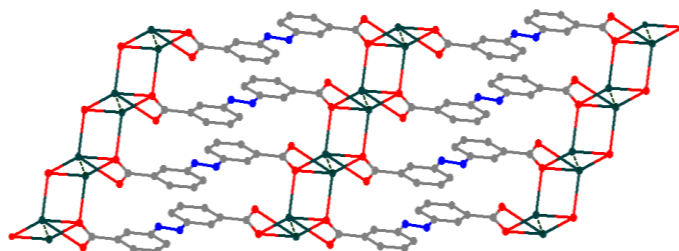


Fig. 1b. 2D network of complex 1 in the *ac*-plane

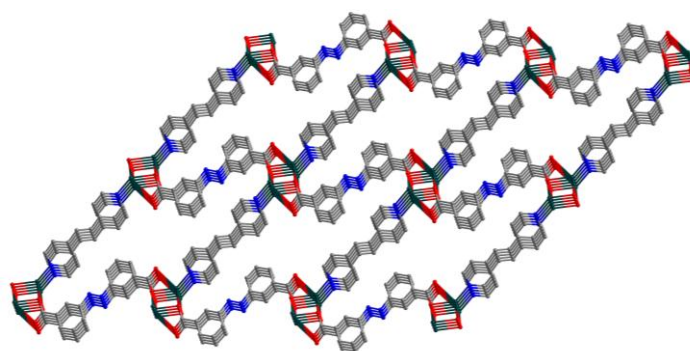


Fig. 1c. 3D network of complex 1

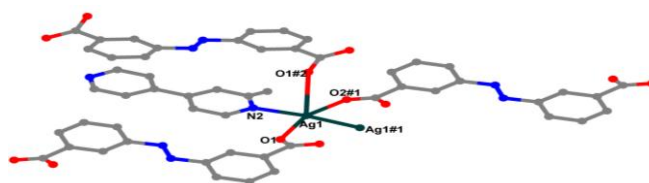


Fig. 2a. Asymmetric unit of CP 2. Symmetry codes: #1: $-x, 1-y, -z$; #2: $-x, 1-y, -z$

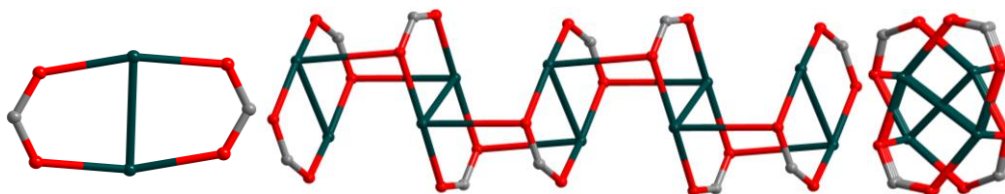


Fig. 2b. 1D chain structure of CP 2

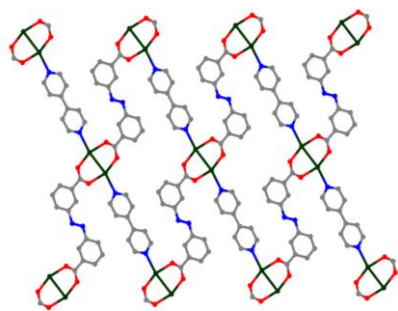


Fig. 2c. 2D structure of CP 2

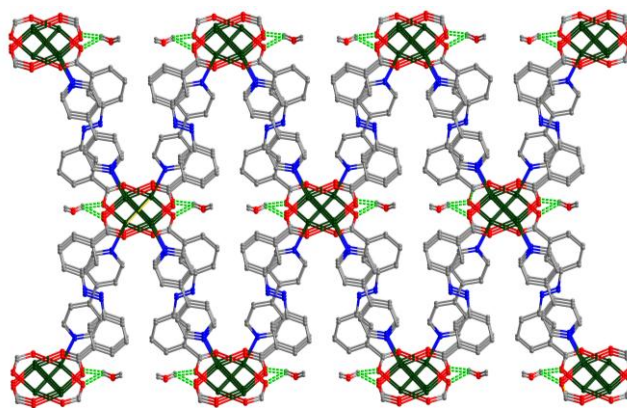


Fig. 2d. 3D structure of CP 2

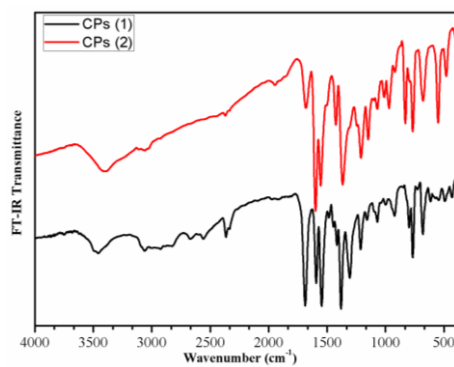


Fig. 3. IR spectra of CPs 1 and 2

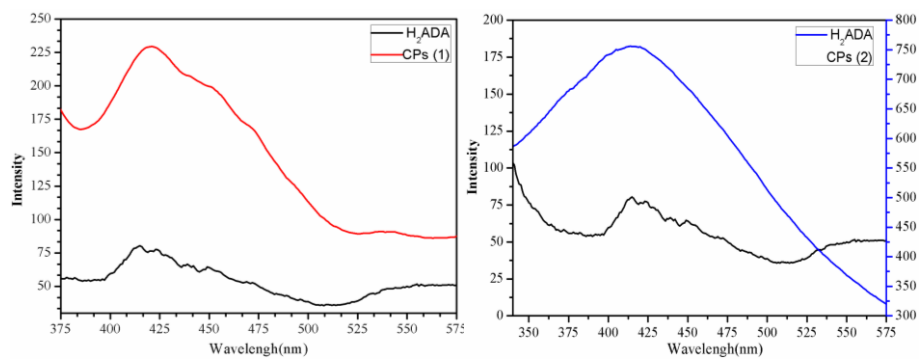


Fig. 4. Solid-state emission spectra of CPs 1 and 2

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for CPs 1 and 2

CP 1					
Bond	Dist.	Bond	Dist.	Bond	Dist.
Ag(1)–O(1)	2.420(3)	Ag(1)–O(1)#1	2.375(3)	Ag(1)–O(1)#2	2.600(3)
Ag(1)–O(2)	2.738(3)	Ag(1)–N(2)	2.243(3)		
Angle	(°)	Angle	(°)	Angle	(°)
O(1)–Ag(1)–O(1)#2	77.11(10)	N(2)–Ag(1)–O(1)#2	91.61(10)	O(1)#2–Ag(1)–O(1)#1	99.81(10)
O(1)–Ag(1)–O(1)#1	102.72(7)	N(2)–Ag(1)–O(1)	137.91(11)	O(1)–Ag(1)–O(2)	50.29(9)
CP 2					
Bond	Dist.	Bond	Dist.	Bond	Dist.
Ag(1)–O(2)#1	2.234(8)	Ag(1)–O(1)	2.241(7)	Ag(1)–N(2)	2.376(9)
Ag(1)–Ag(1)#1	2.892(2)	Ag(1)–O(1)#2	2.913(4)		
Angle	(°)	Angle	(°)	Angle	(°)
O(2)#1–Ag(1)–Ag(1)#1	85.2(2)	O(1)–Ag(1)–Ag(1)#1	77.5(2)	O1(1)#2–Ag(1)–O(2)#1	83.1(3)
O(1)#2–Ag(1)–Ag(1)#1	93.5(6)	O(1)–Ag(1)–N2	88.9(3)	O(2)#1–Ag(1)–N(2)	109.2(3)

Symmetry codes of 1: #1: -x, 2-y, 1-z; #2: 1-x, 2-y, 1-z. Symmetry codes of 2: #1: 1-x, 1-y, -z; #2: x, 1-y, -0.5+z

Table 2. Geometrical Parameters of All Hydrogen Bonds and π - π Interactions for CP 2

D–H \cdots A	d(D–H)/Å	d(H \cdots A)/Å	d (D–H \cdots A)/Å	\angle DHA/°
O(3)–H(3) \cdots O(2)#1	0.85	2.10	2.905(4)	158
O(3)–H(3) \cdots O(2)#2	0.86	1.98	2.887(4)	155
π - π stacking	Cg(i)–Cg(j)	Cg(i)–Cg(j)	Cg(i)–Perp	Cg(j)–Perp
	Cg(1)–Cg(2)	4.1661	3.4277	3.1488
	Cg(3)–Cg(4)	3.9868	3.5629	3.2849

Symmetry codes: #1: -3-x, -2-y, -4-z; #2: -3+x, -2-y, -3.5+z. Cg(1, light blue): C(2)C(3)C(4)C(5)C(6)C(7); Cg(2, lightblue): N(2)C(8)C(9)C(10)C(11)C(12); Cg(3, pink): C(2)C(3)C(4)C(5)C(6)C(7); Cg(4, pink): N(2)C(8)C(9)C(10)C(11)C(12)

Two New Silver Coordination Polymers Constructed from 3,3-Azodibenzoic Acid and Different Pyridine Derivatives: Syntheses, Structures and Fluorescent Properties

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Two New CPs, $\{[\text{Ag}(\text{ADA})_{0.5}(\text{DPE})] \text{H}_2\text{O}\}_n$ (**1**) and $\{[\text{Ag}(\text{ADA})_{0.5}(\text{Bipy})_{0.5}] \text{H}_2\text{O}\}_n$ (**2**), have been synthesized via solvothermal reactions of Ag^+ with ADA^{2-} and/or DPE, Bipy. CPs **1** and **2** were characterized by elemental analyses, IR spectra, X-ray single-crystal diffraction, and thermal analysis. The fluorescence properties of CPs **1** and **2** have been also investigated.

